

DEVELOPMENT OF FAILURE MODEL FOR NICKEL CADMIUM CELLS

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At JPL we have been developing a method of life prediction of NiCad cells during the last four months.

(Figure 5-24)

This is the approach: We are trying to develop an understanding of the mechanisms of degradation and failure, and at the same time develop nondestructive evaluation techniques for NiCad cells.

The mechanisms of degradation and failure involve development of a statistical failure model and also development of chemical or quasi-chemical models of degradation starting with the very basic assumptions of chemical processes leading to failure.

At the same time, we are trying to develop nondestructive evaluation techniques, or NDE techniques as they are called in the trade. Once these are developed, and we do exploratory work, validate them; then they require calibration through real time and accelerated testing so that they can be used to predict usable life.

(Figure 5-25)

This figure shows the approach to failure modeling in greater detail. Test data from Crane and elsewhere in the literature have been used to develop statistical failure models using extreme value statistics. Extreme value statistics is a statistical approach that has been found to be very useful in modeling failure data in widely different systems; for example, transistors, as Dr. McDermott pointed out, and other systems, such as rotors in jet engines.

Extreme value statistics assume that failure occurs in systems due to presence of flaws or defects greater than a critical size. It starts out by assuming or postulating a certain flaw size distribution in the specimen, and this size distribution remains constant as the specimen is aged or cycled. The size of the individual flaws increases as the specimen undergoes aging and as the size of the biggest flaw exceeds the critical area or size failure occurs in the specimen. This statistical approach is therefore different from regression analysis, no matter what our model is. Regression analysis assumes that there is a normal or Gaussian distribution of failure data points across or about the fitting line drawn from whatever model you have. On the other hand extreme value statistics assume that failure distribution is skewed and the underlying flaw size distribution that causes failure is also skewed.

Simultaneously we are working on a cumulative damage model. This starts out with a fairly basic assumption that the flaws, which are supposedly causing failure according to the extreme

value statistics, interact with the electrons to cause damage or increase in flaw size. As this damage accumulates in the battery, it ultimately undergoes failure when the size of the flaw exceeds the critical value postulated above. Electrons here may mean electrons or holes, that is, positively charged ions.

Here I want to emphasize that at this stage of our work — we have been working only a few months in this project — we are not attempting to define flaws. We haven't attempted chemical or physical characterization of these flaws. In fact, there could be many parallel reactions leading to degradation. All we have stated is that there are reactive sites or flaws in the specimen that interact with ions or holes causing damage. Therefore the flaws have two characteristics: (1) they are capable of undergoing a redox process, and (2) they cause failure.

(Figure 5-26)

This slide shows the quasi-chemical model in somewhat more detail. There is an error in this slide. This should be s ; n is the number of charge-discharge cycles, m is the order of reaction, and f is the faradays of electricity passing through the battery. Integrating the rate equation one gets the model.

Now, making an assumption that m is equal to zero, we get the final equation which is our chemical model. This model is based on the one assumption that flaws interact with electrons causing damage and eventually failure. There are two main parameters in the equation; ΔE which is activation energy which defines the temperature dependence, and m , another parameter that describes the rate dependence on DOD. C_0 is the capacity of the battery, and g is a function of charge-discharge rates. We don't yet understand how charge-discharge rate affects life. Now, by keeping everything else constant we can plot the number of cycles or the log of the number of cycles to failure versus the absolute temperature.

(Figure 5-27)

We obtained a fairly good approximation of a straight line, the slope of which is the activation energy. It is about 5.7 kilocalories per mole. This value agrees reasonably well with literature data. This plot was obtained, by the way, by fitting data from the Crane tests. These data are in good agreement with literature which go from about 5 to 7 kilocalories/mole. This value is actually quite low for a chemical process. It is typical of a physical or a transport process. So we get an indication here that probably the rate limiting process leading to failure is a transport process. I don't want to make too much of this, but low activation energy is a clue.

(Figure 5-28)

Once the activation energy was determined, all of the Crane test data (now when I say Crane test data, I mean data based on individual cells, not cell packs), were then normalized to one temperature, 30°C in this case, and then we plotted log of cycles-to-failure versus log of depth-of-discharge. The slope of this line gives the value of m . In this plot, we have fitted both Crane data and literature data in the same line and the fit indicates two things: (1) that the simple model

seems to fit the failure data adequately; (2) the fact that both Crane data and literature data fit not only the same slope but the same intercept in this equation means that there is some internal consistency between the Crane tests and literature data. We also have some points considerably outside the line (this is a log scale) at high depths of discharge. We don't know why these points do not fit this line.

From the slope we determine m which comes out to be 1.5; and the activation energy, as I said before, came to 5.7 kilocalories.

Using these two parameters, all Crane data were then normalized to a given temperature and depth of discharge. We chose 100 percent depth of discharge and 30°C. But any value of DOD and temperature may be chosen.

The next slide then shows application of the Weibull distribution to the normalized failure data.

(Figure 5-29)

Weibull distribution is a given (postulated) initial distribution of flaw sizes in the specimen. The distribution is given in the equation. Beta is known as the Weibull parameter. When the flaw size exceeds c_f , failure occurs. ϕ_f is the cumulative frequency of flaw sizes. Now we can substitute n_f , red for $c_f - c_0$ from the chemical mode. n_f , red is the normalized life frequency.

(Figure 5-30)

The next slide shows a typical Weibull fit. The fit is really quite good. Here we have plotted the log of n_f which is cycles to failure to a population variable which is actually a function of probability of failure. The slope of this line is beta, the Weibull parameter, which defines the initial distribution of flaw sizes, which must be constant if the Weibull model is applicable.

The test whether this failure model applies to this system is whether beta remains constant, in other words, if the fit is linear. And here we find that for very large variations of depths of discharge, temperature and other variables, beta is constant. These data have been segregated according to charge-discharge rates since we don't yet know how charge-discharge rate affects life. We can say however that the effect is small.

From this intercept we can calculate the most probable reduced lifetime, extrapolated to 30°C and 100 percent depth of discharge. Using this model we can calculate the most probable reduced lifetime for any condition such as 20°C and 20 percent depth of discharge, by simple substitution to that algebraic equation that I showed.

(Figure 5-31)

The next slide shows another Weibull fit for the 4C:C/2 charge-discharge rate. Again the fit is pretty good, and the reduced lifetime is obtained from this intercept here.

There are some scattered data that show pretty significant deviation, and these are the same data points that also showed deviation in the equation where log of depth-of-discharge was plotted versus log of cycles-to-failure.

(Figure 5-32)

The next slide shows another set of data fits for this charge-discharge rate $C:C/2$. This is the beta value that can be obtained from the slope, and it turns out that the beta value is fairly independent of CR or DR. It varies from about 2.5 to 3.5 no matter what the charge-discharge rate is. This is one of the most promising aspects of this attempt to apply failure models to this system; the fact that the value of beta remains constant over even widely different charge-discharge rates as well as temperature from 20 to 50 degrees, depth of discharge from 20 percent to almost 100 percent.

(Figure 5-33)

The next slide shows another such fit. In fact, we have fitted most of the Crane data, 360 data points to four of these Weibull plots. There are 75 points in each of these fits.

One of the things that I wanted to mention before I go into our description of our work on development of NDE techniques is something which relates to a question that was asked Dr. Landers. The question was, does the lifetime or cycle life depend on the cycle period, or does it just depend on number of cycles?

The answer from our model as well as the test data is that life is limited by the number of cycles rather than dependent on the time during which those cycling tests are carried out. This indicates very strongly that the rate limiting process causing failure is a transport process. Because, if life was limited by any other factor such as a chemical process, then there would be a strong dependence on the actual time spent in testing.

And this again, therefore, reinforces our view that the rate limiting process is probably a diffusion controlled process or a transport controlled process, which we can speculate could perhaps involved diffusion across the double layer or whatever. These types of speculations, therefore, indicate what kind of mechanistic investigation, such as surface characterization, spectroscopy, etc., that would be appropriate to do on these electrode surfaces, and the double layer.

(Figure 5-34)

The next slide shows another bit of information that we obtained from our model. It turns out that reduced most probable lifetime – remember now that the reduced lifetime is the normalized most probable life expectancy of the cell – depends on the cell capacity and number of plates.

So, using this equation and knowing the value of beta, we can predict how life will decrease or increase or change as the cell capacity changes.

This model predicts that the life, most probably reduced lifetime, life-cycle expectancy should decrease as the number of plates increase, or the capacity increases in the cell. This, of course, is a testable prediction.

(Figure 5-35)

The next slide shows what we have been trying to do in developing nondestructive evaluation techniques. We have been measuring complex impedance on sealed NiCad cells. Complex impedance has been applied before to NiCad cells, so I don't really want to go into it in great detail.

This is a plot of the imaginary part of the impedance, or the reactance versus the resistance, the real part of the impedance. R_s is the solution resistance. The height of this point gives the double layer capacitance, and the diameter of the half circle here gives the resistance of the charge transfer resistance, and the slope is the Warburg impedance which is related to the diffusion across the double layer. When we applied this technique, this is the shape of the curve we would expect if this simple equivalent circuit is a good assumption.

(Figure 5-36)

The next slide shows the results when a fully discharged NiCad cell was used to measure complex impedance. When the cell is fully discharged, only the cadmium electrode had any capacity left, and therefore we are really measuring the cadmium electrode alone because the nickel electrode acts like a very large capacitance and is shorted out at high frequencies. The results show a fairly good approximation to this very simple model that was used to model the cell behavior, and from this slope of the linear portion we can calculate the diffusional impedance. The objective now is to measure these parameters such as the reactance and the resistance as a function of cell cycling. That is to say, we would like to cycle the cells to various numbers of cycles under given temperature and DOD and see if we can detect any changes in impedance parameters.

This would be a completely empirical approach trying to find out if we can correlate any of these parameters, for example, the charge transfer resistance, or the double layer capacitance to the cell life. And if there is a correlation, then we may be able to predict the life of that particular cell or cell pack.

I think this is an important objective because even if we have very accurate life prediction models, they still will give us a certain probability of life for a population of NiCad cells and what we really need to know is the life of a particular pack that goes up in a certain spacecraft. Therefore, if we can come up with an NDE technique — and I might be unduly optimistic about that possibility — we would be able to then actually predict life of a particular cell pack. If this is possible, we can probably fit the measurement into an assembly line as a quality control procedure.

(Figure 5-37)

The next slide shows plots of diffusion of impedance and they are calculated, actually. But the value of diffusion impedance in this cell, Warburg impedance is a function of when it is fully discharged.

(Figure 5-38)

The next slide shows the data obtained when complex impedance measurement is carried out on a partially charged cell. The data now is a lot more scattered and is much more difficult to interpret. This is more or less where we are. One of the several other possible diagnostic approaches we might take is to put in a third electrode in the system so we can treat each of these plates separately.

DISCUSSION

LANDERS: I think that these three papers showed a process of growth and sophistication of data treatment. We older types look at pictures, and I will have a little bit more to say about that.

First of all, I have these comments: The design variables which were considered on this turned out very happily, from the manufacturer's point of view, because they showed that a lot of his manufacturing processes in terms of the three variables that were looked at, do not have to be held too closely in the manufacturing process.

Second, the percent DOD function which I used comes from very simple theory. Actually, it is arithmetical in nature. What it comes from is that supposing you are running an 80-percent DOD. That means you can only have 20-percent degradation before failure.

On the other hand, if you are using a 20-percent DOD, you are going to have 80-percent degradation before failure.

It is that particular fact that results in the DOD function which I used. Intuitively it has got to be so simple that it ought to be a close approach.

The temperature function is very important, obviously, in predicting those low temperatures. First of all, in the empirical equation which I used there, I was trying to fit a 50° C data point.

Obviously using trebling as a temperature effect is going to lead to very high temperature cycle-life values at the low temperatures, and I don't believe that myself.

The theoretical equations which I finished with in my talk used doubling, and this does not quite fit the 20° C point.

As you may recall, my doubling equation showed it to come out about 10,000 cycles lower. What this means is if the so-called theoretical equation is a better fit than whatever the actual situation may be at low temperatures, the theoretical equation is going to predict much lower values of cycle life at lower temperatures.

Finally, I can't agree with Pat about the temperature functions of linear, and I think your data indicates that also.

GUPTA: Temperature functions almost always have to be exponential, because whether we have a physical process or a chemical process, usually there is an activation parameter. It is difficult to come up with a molecular level understanding of a process that varies in any way with temperature other than in an exponential manner. This is because this exponential temperature parameter is related to the Boltzmann distribution.

May I just summarize a little on the DOD. The model that we used for treating DOD is that the DOD tells us how many electrons are passing through a cell, and therefore how much charge is being transported, and therefore that determines the number of moles reacted. And here we expect a polynomial dependence. Now whether it is to the power of 1 or to the power of minus 1 — for example, Dr. Landers says it is to the power of minus 1 — or it is to the power 1.5, we don't know for certain. Our model, used to fit the data from Crane, gives 1.5 to perhaps plus or minus 10 percent accuracy.

This result has implications about the nature of the reaction that is going on. In other words, it tells us the molecularity of the reaction, and it is difficult again to understand the value of less than 1, unless we are talking about a rate limiting process that has nothing to do with the movement of charges in the battery. Therefore, we expect n to be higher than 1, and we expect them to be less than 2, because if n was more than 2 it means physically that two or three electrons must converge to a site before carrying out a reaction, which is an unrealistic expectation. So physically it makes sense to have it between 1 and 2.

McDERMOTT: I'm not suggesting that the temperature dependence of chemical reactions is linear. That's not what I'm saying.

I'm saying that the cumulative effect of all the reactions going on in the cell has a certain effect on life. We are not looking at the cell. It is just an electrochemical experiment. We are trying to say what is limiting the life and what's the functional relationship.

When we take Crane data, we find over the limited range we are dealing with, that if you just plot temperature versus — with everything else held constant, you will find it approximately linear.

Sam, didn't you do that?

LANDERS: Yes.

McDERMOTT: You found up to a certain point, 50 degrees, that you do have this. Now you might have some very interesting things happening below 20 and to zero that are not linear, so that extrapolation in that range is very tough.

I would like to ask you, did you make any prediction of the low temperature and lower DOD cycles to failure based on your equation?

GUPTA: Yes, I did. But let me first clear up this temperature debate by saying, I think Dr. McDermott's approach and our approach are complementary.

You are trying to fit the data as you see with temperature, and the linear fit seems to do a good job or adequate job.

What we are trying to do is go beyond this fit, at least in terms of our program. We are trying to use this test data to develop an understanding of failure mechanisms. As soon as we try to do that, we have to have some kind of an idea about an activation energy, because that gives us some kind of information about the chemical changes that are going on which lead to failure.

Therefore, I think that both of these approaches can be used. If you use Dr. McDermott's approach within its limits, it may be just as well. Yes, we have made predictions. This is what I mean by most probable value of reduced lifetime.

(Slide)

From this intercept here, we can calculate, for example, the most probable life of the battery under various conditions. And it turns out that this is about 1420 cycles. That's at 30°C and 100-percent DOD. This is an extrapolated value or normalized value.

So we go to 20-percent DOD, we just apply the algebraic factor, 500 divided by 20 to the power 1.5 to this number. We multiply it by that and then we apply our temperature dependence parameter, which we have deduced from the data, which is E to the power minus 5.7 divided by two times whatever temperature we have. If you work it out — in fact, I did do one calculation — it turns out to be roughly 7.5 or 8 years of cycle life. It is a fairly trivial calculation to perform, so the information is right here.

GROSS: Please explain the ordinate and axis on that figure.

GUPTA: This is n_f , the number of cycles to failure reduced to normalized using the chemical equation. If you want to see it, I can go back to the previous slide. This is P of n_f reduced. This is a population variable, and this is a function of what I call $\Phi(n_f)$ which is the cumulative frequency of failure or probability of failure at n_f . The quantities are derived by using standard statistical techniques. What we do is to list the number of cycles to failure and give them integral labels like 1 to l ; for 76 cells, there would be 1 to 76.

Then, suppose we have n_f for the i th number in this series, so that then P would be i over l plus one.

In other words, if you take the highest number, then P would be L divided L plus one. This is an arbitrary but accepted procedure which is used to estimate probability of failure, $\Phi(n_f)$. This is available in any textbook on reliability theory.

HENNIGAN: The initial purpose of the test as we set it up was to see if we could get some profiles in, say, a week or two at the parameters we ran to tell you whether we had good cells or bad cells. But I was a little dubious of that.

At least, we thought maybe we could get something in about a month or two: an accelerated test that we could take a sample from a lot, let's see, yes, we got good cells and bad cells, but it appears that it is coming along pretty good. I think Pat said it looks like given a six-month period we could test cells and determine whether they are good or bad.

Now I understand that there has been some disinterest in this program at the levels that be. And I was just wondering if someone would want to comment on that?

LANDERS: One more comment. I think that Pat has done us a great favor in iterating the lessons we have learned from this test, in view of, well let's say, the philosophy of accelerated testing.

GROSS: My understanding when the test was in progress was that there was a possibility that data could come out of the test to give an indication of when failure would happen prior to actually getting the failures.

In the analyses we have seen today, correlations show essentially how you could set up a test, but you would have to run the test to complete failure.

So the question is, were there any kinds of predictors that were determined during the test to either be valid or invalid to predict when failures might be because of voltage degradation and other things?

GUPTA: I would like to add a comment to that. That is the purpose of our work on trying to develop NDE techniques. I think that using electrical properties of cells such as cell voltage to predict its life is not going to work.

We think that the only way we can really predict life of a particular cell pack and not of a population is to make some kind of nondestructive measurements of properties which are different from the properties we are measuring when we are following degradation of properties. We think we have to make measurements of special properties, using nondestructive evaluation techniques which will eventually correlate with life.

McDERMOTT: We tried to look at that in terms of the analysis of end-of-discharge voltage, end-of-charge voltage, things like that, the slope of the discharge curve at half capacity. And I would say we have not done a thorough analysis of that part of it.

One of the problems was that we had so much data, and that was one of the reasons for getting a reduced, edited version of the data, in order simply to attack the problem. What we have done is try to take 30 representative cycles out of the whole lifetime of the cell. All right. This would be clustered more at the beginning of life and more at the end of life. And then to try

to analyze various parts of the discharge curve, the shape or the knee right as you start to discharge, the slope of the discharge curve as a rate of voltage change and so on.

I would say that is still in the future in terms of using that for predicting what you were talking about. One of the problems is, once the cell goes into sort of an equilibrium type test phase, initially you will go through some changes in these parameters, then it will flatten out, and it will go like that for years on a relatively mild cycling condition. And you don't start seeing warning signs until you are almost at failure, unfortunately.

So, I would say it's a very sensitive, the voltage changes and so on, issue that we are still pursuing. One problem we had is when you look at one voltage curve, you tend to have fluctuations in other parameters that throw you off. For example, if you look back at the temperature data, the box might have changed temperature a few degrees and so on, or the night before the lights went out and they stopped the test and they started back up again, so it is going through one of those equilibrium problems again.

So it is not an easy thing, but what we are trying to do is attack it by looking at 20 to 30 representative cycles. Now when I say that I'm saying we are taking a cluster of cycles, three cycles, and averaging them together. For example, cycle 25, 26 and 27, and then 50, 51, and 52 and so on, and then averaging clusters of those to try to work out some of these ripple effects of just selecting one cycle which could have some other influence in it.

We are still working on it, but we are probably a little further off from that than we are from the other analyses. But I think, ultimately, that is going to be the best test when you can look at the voltage and see some of those changes. That's the best nondestructive means I think we have at our disposal, since you get telemetry from the spacecraft, in order to look at the voltage and run a profile and so on and see if you can predict how long it has got to go.

LACKNER: I'd like to get a bit of clarification on your complex impedance diagram, particularly what was the significance of Zed double prime, or Z'' ?

GUPTA: The Z' prime is the real part of the impedance. The Z'' double prime is the imaginary part of the impedance.

LACKNER: What does that mean in English?

GUPTA: It probably means Z' prime is resistance, and Z'' double prime is the reactance. In other words, if you write the impedance as a complex number, $A + jB$, then the coefficient of j is the Z'' double prime, and the real part which is A , is Z' prime. It is measured as a function of frequency, and this is one area where we have done things slightly different from that that has been reported in literature.

We have looked at a very wide range of frequencies. So we just measured this impedance as a function of frequency.

LACKNER: I can follow the impedance as a function of frequency.

GUPTA: Can we go forward to the slide?

(Slide)

What we are trying to do is to measure the slope of this line.

(Slide)

Here is the real data, and we are trying to measure the slope of this line, the height of this circle here, the extrapolated semicircle, and looking at its diameter. If you go through the math — and I must say that I am not an expert at complex impedance so I would not be able to give you the equations here, but they are available — this diameter would be called the charge-transfer resistance. In other words, these have physical meaning as far as the cell is concerned, as long as you equate the cell to that equivalent circuit that I proposed, which is, admittedly, an oversimplification.

LACKNER: I guess what I'm trying to get at is what the physical meaning is of those curves?

GUPTA: I really cannot make any statements about that precisely, because I think that the equivalence of the cell to the equivalent circuit is a very tenuous assumption. Our purpose here is fairly limited. We really want to do an empirical correlation here.

If you want to make that assumption that the equivalents of the cell here to the equivalent circuit is good, then these parameters acquire physical meaning. For example, the height here is equivalent to the capacitance of the double layer. The diameter here is equivalent to resistance of charge transfer.

But it really will not be the case in the real cell because the equivalence itself is really not very good. We are really pleasantly surprised that it does show this type of behavior, which is roughly what we would expect.

LACKNER: The reason I find this interesting is in some of our tests with actual flight satellites, and on the ground-simulated satellites, we find that as they age and as they deteriorate, you get an increase in the internal resistance. Particularly, between charge and discharge, they can vary from 5 milliohms to 60 milliohms.

GUPTA: This is precisely the kind of properties we would like to measure. We are planning a test program, where we will cycle cells, flight-quality cells, and measure these as a function of sub f divided by 5, and sub f divided by 4, 3, 2, 1 and at failure, and we will see if there is any correlation.

We would also like to do other things. For example, we would like to take a cell to a certain state of charge, equilibrate and apply a pulsed current to it. Basically it is a charge efficiency measurement and we would like to see at what point of charging level there is an irreversibility, and whether this irreversibility is growing as a function of aging and so on.

So yes, answering your question, I think that it will show up in this type of an analysis.

LACKNER: Just one general observation I would like to make of the whole area of accelerated testing is, it appears we are doing accelerated testing on completed cells.

Now if you are in a procurement program for a satellite, by the time you have a completed cell it is pretty sad. You have to really have a good idea of what to specify for your cell and have accelerated programs on components, so you can sort of say yes, we know these components and how you put them together will give us good life.

Is there any program along that line?

GUPTA: Speaking only about the JPL program, yes, there is. There is a parallel investigation about components and cells.

BETZ: Do you have a comment?

LANDERS: Yes. Along those lines, Joe, there is a mechanical engineer in our shop named Dr. Fritz, and he is approaching things from the point of view of a mechanical engineer and is looking for possible mechanical means of failure of these things. He is coming up with some very interesting results which I hope will soon get into the literature.

One other thing, along the lines of the question that Sid Gross asked, and maybe others, there was an attempt made to look at the manufacturing data for the Crane program in terms of what is called pattern recognition techniques by Perrone and Company at Purdue.

This has been published. When I read that paper, I really didn't see that it told us a lot, but it did say one thing, and that is the low capacity cells are likely to fail first.

McDERMOTT: I have one comment on Joe Lackner's trying to find an accelerated test for components.

I think this is good if you keep in mind that the proof is in the pudding. When you put everything together, it is the system that is going to fail. In the failure modes that we have looked at, it is the interaction of the various components in the cell that ultimately leads to death. So you can't rely too much on simply testing one component and then trying to put it all together in a mathematical model. You can't rely on that solely. You have to get it all in that can with so much electrolyte and see how the system fails.

DYER: In the impedance work, I find it difficult to understand how you can pick up defects in a cell based on the measurements you are making. Warburg impedance and capacitance are very insensitive to the small defects you were talking about before. Do you have a plan here by which you can be sensitive to these defects?

GUPTA: I'm sorry if I gave the impression that we are looking for or trying to characterize defects using our nondestructive evaluation techniques. I want to emphasize that the NDE that we are trying to do involves a completely empirical approach right now. If we can come out of it with some physical-chemical characterization of the defects, that would be purely a bonus.

I don't think that the Warburg impedance and the reactance, etc., are going to tell us anything about defects. The most we are hoping for from the impedance measurements is that, for example, the Warburg impedance might change as the cell undergoes cycling.

For example, we find — this is very preliminary work and I didn't really want to present it — it undergoes some change as the cell undergoes cycling, but we don't know if that effect is real yet.

As far as the defects are concerned, we do have a test plan to characterize or understand what these defects are. This work will involve spectroscopy, that is, surface spectroscopy. For example, we would like to see if there are ions that are capable of multiple oxidation states since we find that electron interaction seems to be rate limiting. We would like to find out if we can identify or characterize these sites, for example, nickel+4 or cadmium. Auger scanning, Auger spectroscopy, and perhaps resonance Raman spectroscopy may be carried out now that we have some ideas. In other words, we could not have done resonance Raman spectroscopy on these electrodes, not knowing anything about what the rate-limiting process is. For example, if it turned out that the rate-limiting processes causing failure are physical processes that have zero chemical order of reaction, then there would be no point in doing chemical characterization of the electrode surface.

But it appears as if the rate is transport controlled and the failure has been caused by interaction with electrons or ions. What is more, the model is zero order with respect to defects, which strongly indicates that the defects are on some surface. Therefore, it makes some sense to use surface spectroscopy on the cell components, and I wouldn't be surprised if some of the spectroscopic results correlate to failure.

DYER: I have a second comment then. Your data seems to show it is a transport-limited, low-activation-energy, time-independent process. And yet your model is a defect-growing process with time. I imagine it would also be a high-activation-energy process.

How could you reconcile these two?

GUPTA: We have a sequence of processes, ions being transported to the defect site, and in the defect site interacting with ions or electrons. The reaction of the defect site with electrons has high activation energy, but proceeds at a very much faster rate than the transport rate of the electrons and the ions to the defect site. In other words, although the reaction that causes degradation and failure is a chemical reaction, it is not rate limiting. So any time you monitor failure or degradation, you will be picking up the slowest rate, which is the transport process. In fact, in electrochemistry, often transport processes are rate limiting, no matter what electrode reaction is going on.

THIERFELDER: I want to comment on the suggestion Dr. Landers made using a 45-minute orbit instead of a 90-minute orbit. A lot of tests were run in three-hour orbits. When I compared the results of the three-hour orbit with the one-and-a-half-hour orbit, they were identical results.

GUPTA: This is what our results show. I think it is cycle-limited and not time-limited.

APPROACH

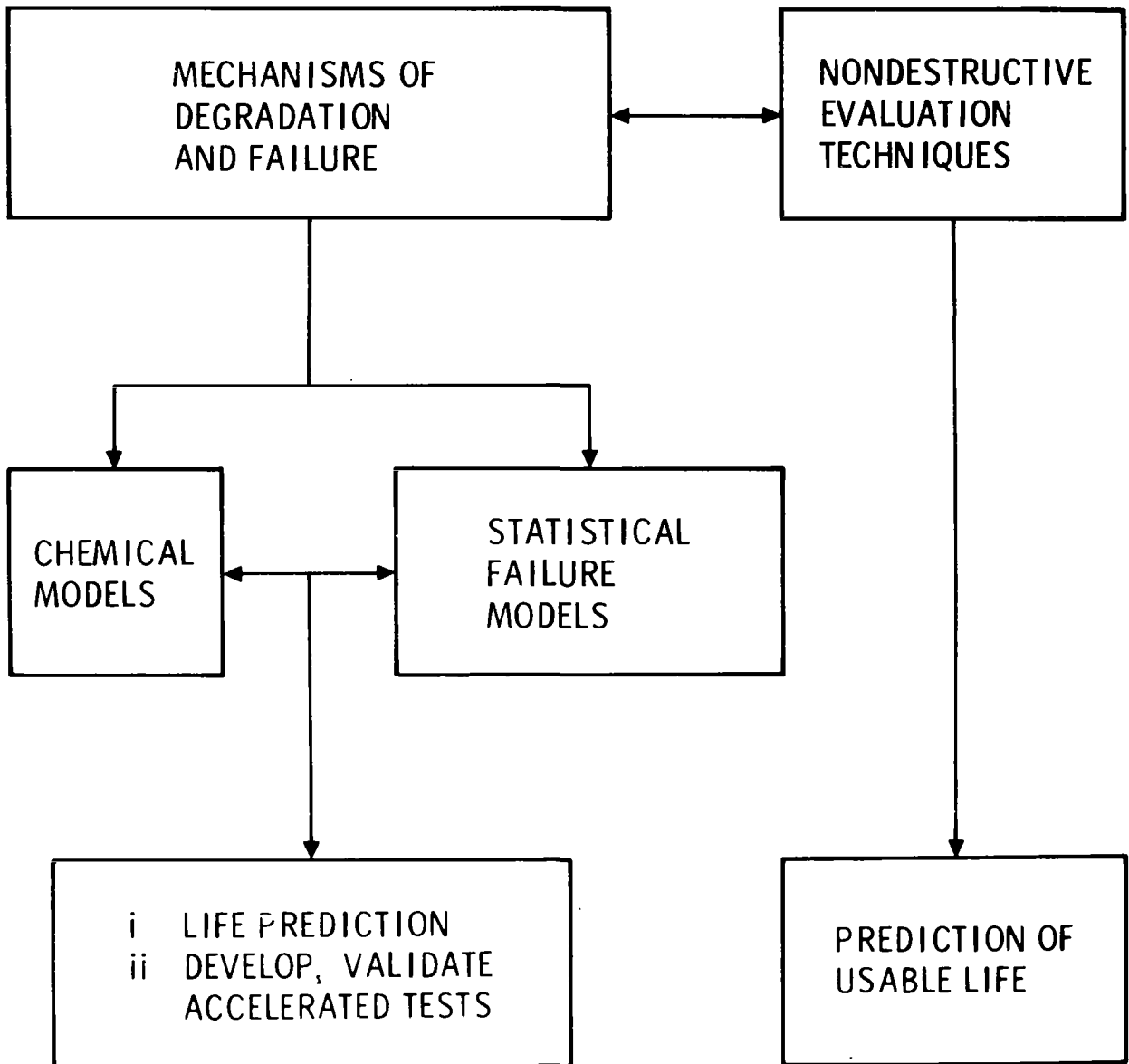


Figure 5-24

DUAL APPROACH TO FAILURE MODELING

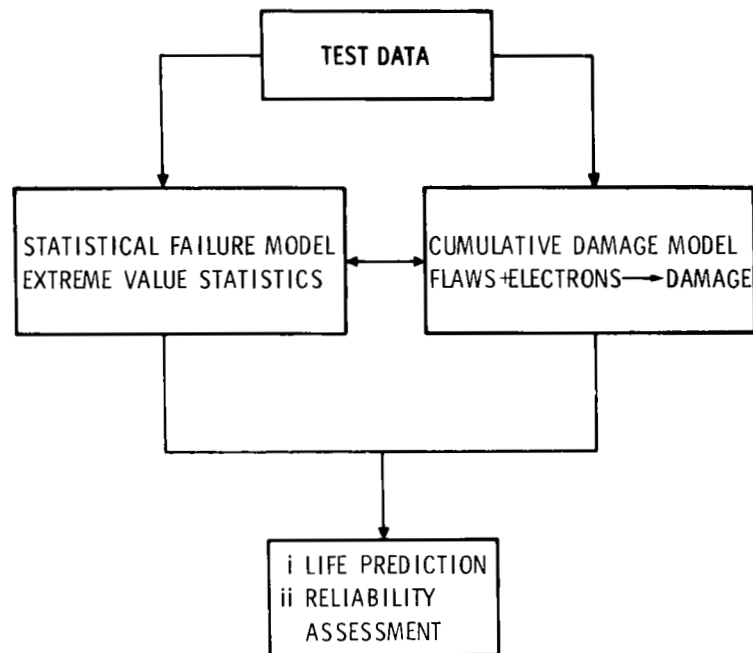


Figure 5-25

QUASI CHEMICAL MODEL

FLAWS + ELECTRONS → DAMAGE

$$\frac{dc}{dn} = kf^m c^5$$

WHERE f = NUMBER OF FARADAYS OF ELECTRICITY PASSED

c = AREA OF FLAWS

$$n - n_0 = \Delta n = \frac{1}{kf^m c_0^{s-1}} \left[\frac{\Delta c}{c_0} - \frac{s}{2} \left(\frac{\Delta c}{c_0} \right)^2 + \frac{s(s+1)}{6} \left(\frac{\Delta c}{c_0} \right)^3 \dots \right]$$

$$c_f - c_0 = n_f k_0 (\text{DOD})^m c_0^m g^m e^{-\Delta E/RT}$$

WHERE c_0 IS RELATED TO PLATE CAPACITY

g IS RELATED TO CHARGE, DISCHARGE RATES

DOD IS DEPTH OF DISCHARGE

ASSUMPTION : FAILURE OCCURS WHEN $c = c_f$

Figure 5-26

DETERMINATION OF ACTIVATION ENERGY

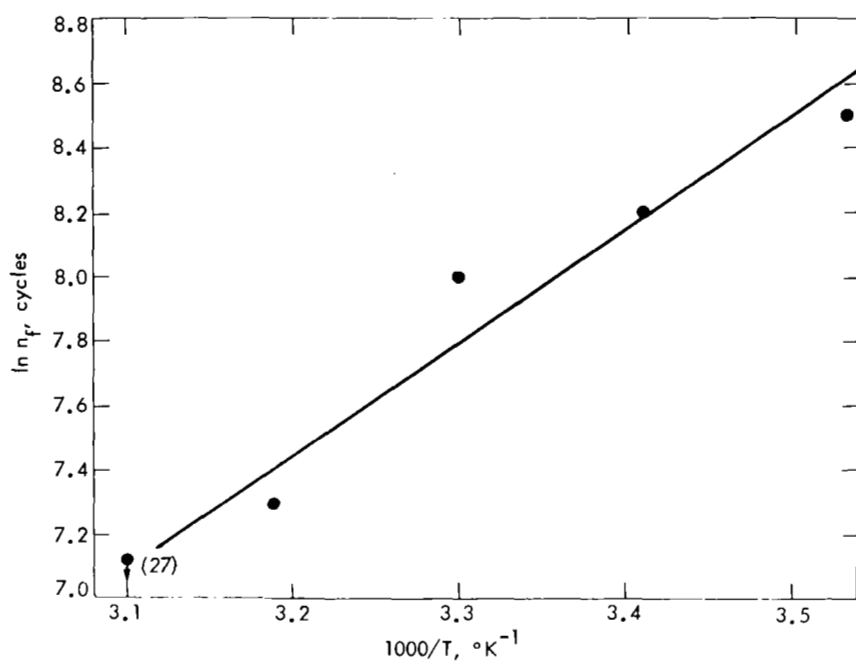


Figure 5-27

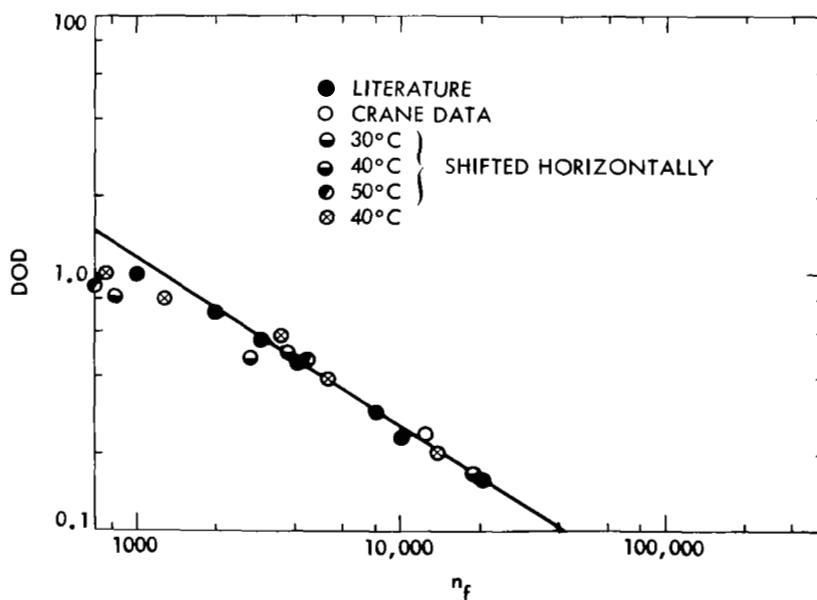


Figure 5-28

STATISTICAL FAILURE MODELING

WEIBULL DISTRIBUTION

$$f(c_0) = \beta (c_f - c_0)^{\beta-1}$$

$$\phi(c_0) = 1 - \exp \left[- \left(\frac{c_f - c_0}{c_f - c_0^*} \right)^\beta \right]$$

$$\phi(n_f) = 1 - \exp \left[- \frac{n_{f, \text{red}}}{n_{f, \text{red}}^*} \right]$$

$$\text{WHERE } n_{f, \text{red}} = n_f k_0 (\text{DOD})^m c_0^m g^m e^{-\Delta E/RT}$$

Figure 5-29

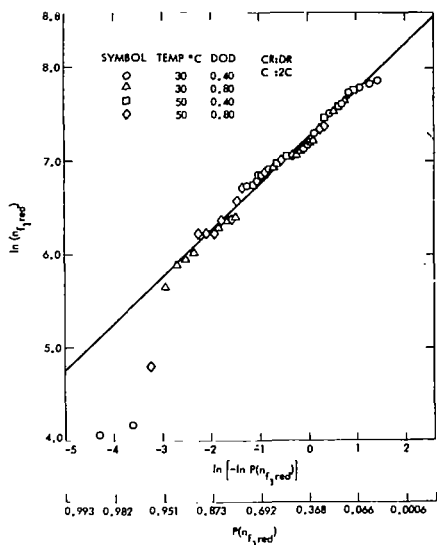


Figure 5-30

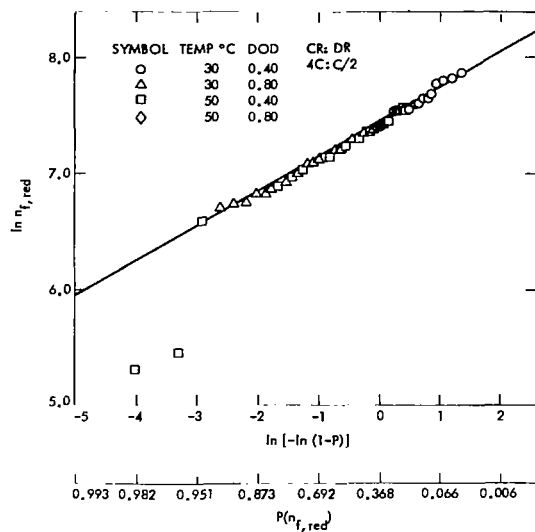


Figure 5-31

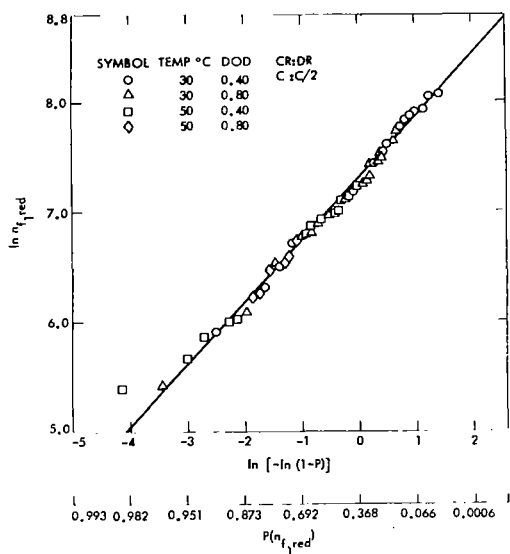


Figure 5-32

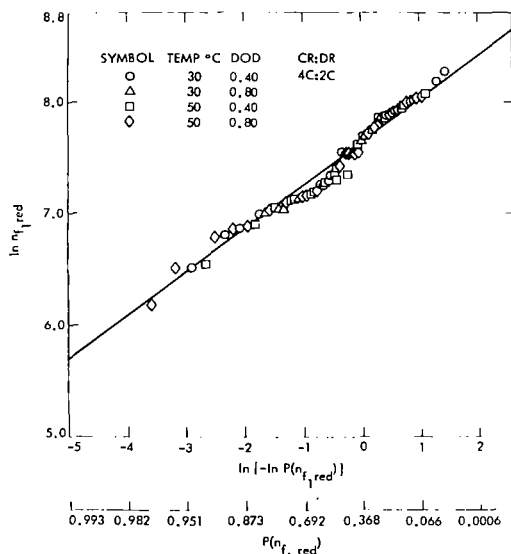


Figure 5-33

$$(N_{F, RED})_2 = (N_{F, RED})_1 (V_1/V_2)^{1/\beta}$$

WHERE $(N_{F, RED})_1$ AND $(N_{F, RED})_2$ ARE
MOST PROBABLE REDUCED LIFETIMES FOR CELLS OF VOLUME V_1 AND
 V_2 RESPECTIVELY.

THIS TECHNIQUE THEREFORE CORRELATES CELL LIFE WITH CELL SIZE AND,
IF VALIDATED, WILL ALLOW LIFE EXPECTANCY TO BE FACTORED INTO DESIGN OF
POWER SUPPLY OF SPACECRAFTS.

Figure 5-34

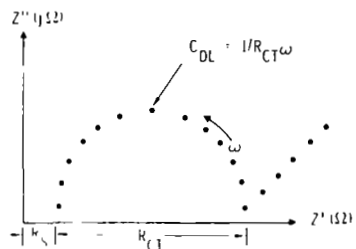
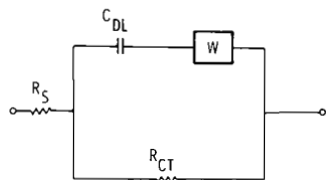


Figure 5-35

COMPLEX IMPEDANCE DIAGRAM

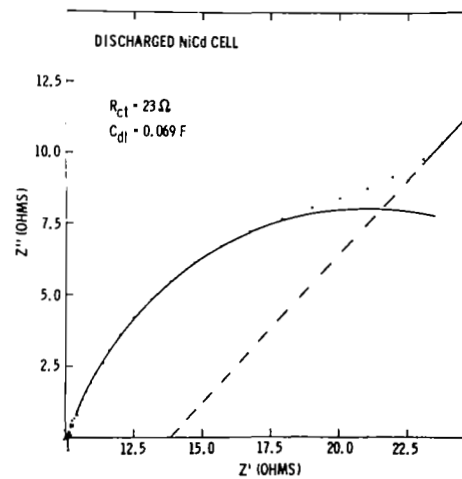


Figure 5-36

COMPLEX IMPEDANCE DIAGRAM

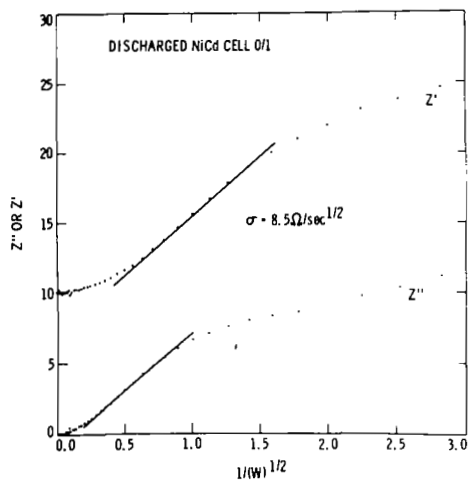


Figure 5-37

COMPLEX IMPEDANCE DIAGRAM

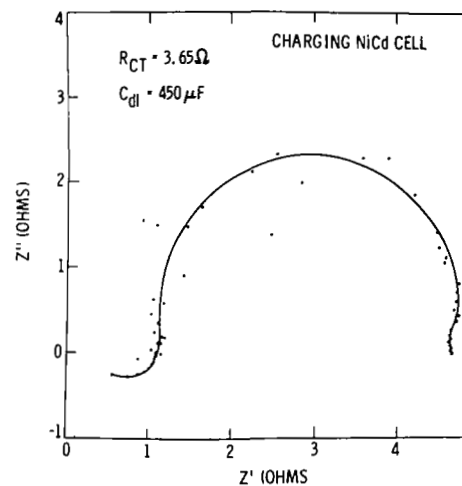


Figure 5-38